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Macromolecular compounds

Field of invention

The present invention relates to new photoinitiators capable of acting as photocrosslinkers providing a combination of photoinitiating and crosslinking processes.

Background of invention

The UV curing of resin formulations is widely used in industry as the setting process for coatings, adhesives, and more recently paints. Such formulations may comprise a combination of vinyl, usually acrylate, monomers and crosslinkers, together with a photoinitiator. Other possible constituents of the formulations include crosslinkers and vehicles. In general an advantage of photocurable formulations is that the monomers act as their own vehicle, and the use of solvent is obviated, which has environmental advantages.

Advances in the technology of photocuring, improvements such as, those in UV lamps, cationic initiators for epoxide-based formulations, water borne coatings, and many novel monomers has enabled this production process to penetrate a number of important manufacturing sectors. Photopolymerization is now used in photoresists for printed circuits and microelectronics, for photolithography, magnetic recording media, glass-fiber laminates, and for medical devices, especially for dental and ophthalmic applications.

For the medical applications of photopolymerisation it is usual to employ visible light, rather than UV, to effect the cure of the resin formulation. The use of visible, usually blue, light avoids exposing patient and dentist or surgeon to harmful irradiation. Increasingly the merit of this approach is being recognized for industrial practice, where operatives also need protection from prolonged exposure to harmful UV.

It is a characteristic of almost all, if not all, of the formulations used for aforementioned types of application that they are crosslinked. Crosslinking of the polymeric bases which constitute the coatings or artifacts of the aforementioned industrial products confers important advantages upon them. Crosslinked polymers have greater environmental (e.g. temperature

and moisture) resistance, solvent resistance and dimensional and mechanical stability, than equivalent linear polymers. This is especially so for where the equivalent linear polymer are produced by photopolymerisation they have an atactic, non-crystalline, structure.

Crosslinking is introduced into photopolymerized products by including in the formulation for the resin, coating or gelling system, an acrylate, or similar, crosslinker, which is characterized by having two or more crosslinkable acrylate or vinyl functions. In some formulations this crosslinking species is a polymer of low molecular weight. The crosslinker copolymerizes with the monomers of the formulation to produce a network structure.

It is the object of the present invention provide compounds which act as photocrosslinkers for vinyl, acrylate and methacrylate monomers and acrylated silicone compositions, especially in solution.

It is also an important object of the present invention to provide photocrosslinkers with capability to act in aqueous solutions, especially on water soluble macromolecular particles having functional groups for crosslinking.

It is another object of the present invention to provide photocrosslinkers with enhanced photoactivity (100 % conversion of monomer to polymer in aqueous solution) which reduces photoinitiator residues to a minimum, especially, vinyl modification of photoinitiator component and thereby reducing compositional drift, Draize and other environmental hazards.

The invention as presented below will explain how the mentioned objects are met while discussing further obvious advantages.

Description of the invention

The photoinitiators according to the present invention can be described according to the general formula $(A)_n (B)_m (C)_p$. They are capable of participating in a crosslinking photoinitiated reaction with a substrate having groups active for crosslinking and A, B and C are units either of substituted ethylene groups or substituted siloxane groups in the macromolecular structure, wherein units A, B, C do not have same substitutions and the unit C is linked to a photoactive group which generates radicals retained on the macromolecular photoinitiator when exposed to light at a determined wavelength in order to accomplish a crosslinking

reaction with the substrate. The molar relationships between n, m and p in the general formula are n = 0-98 mole %; m = 0-98 mole %; n + m = 50-98 mole % and p = 0.5 - 50 mole %.

Preferably, photoactive group generates free radicals by irradiation of light having a wavelength above 305 nm. For this purpose the photoactive group comprises a phosphorous atom, suitably linked to units C by an acyl- or aroyl group. Preferably, the links to the units C comprise an optionally substituted phenylene group.

According to preferred aspects of the present invention, the above mentioned units A, B, C of the macromolecular photoinitiator structure are:

A= $-CH_2-C(R^1R^2)-$ or $-Si(R^1R^2)-O-$;

B= $-CH_2-C(R^1R^3)-$ or $-Si(R^1R^3)-O-$; and

C= $-CH_2-C(R^1R^4)-$ or $-Si(R^1R^4)-O-$

wherein,

R^1 is hydrogen or methyl when A is $-CH_2-C(R^1R^2)$, B is $-CH_2-C(R^1R^3)-$ and C is $-CH_2-C(R^1R^4)-$

R^1 is $-CH_3$ if A is $-Si(R^1R^2)-O-$, B is $-Si(R^1R^3)-O-$ and C is $-Si(R^1R^4)-O-$;

R^2 is $-CON(Me)_2$, $-CO_2CH_2CH_2OH$, $-OCOCH_3$, $-OCOCH_2CH_2Ph$, -OH or a lactam group when A is $-CH_2-C(R^1R^2)-$;

R^2 is methyl or phenyl when A= $-Si(R^1R^2)-O-$;

R^3 is $-CON(Me)_2$, $-CO_2CH_2CH_2OH$, $-OCOCH_3$, $-OCOCH_2CH_2Ph$, -OH or a lactam group when B is $-CH_2-C(R^1 R^3)-$ with the proviso that R^2 and R^3 are not the same;

R^3 is R^1, R^2 or $-CH_2CH_2CF_3$ when B is $-Si(R^1R^3)-O-$;

R^4 = -PhCOP(Ph)(R^5)=O or -PhP(R^5)OC(Ph)=O wherein R^5 = phenyl, 3,5-dimethylphenyl, 3,5-dimethoxyphenyl, 3,5-dimethylolphenyl or styryl.

It is to be understood that the siloxane backbone containing

macromolecules are aimed to be used in silicone based systems.

The inventive macromolecular photoinitiator which also acts as a crosslinker is hereinafter termed a photocrosslinker. The photocrosslinker provides a combination of photoinitiating and crosslinking processes. It is an important feature of the present invention to effect this combination of function by attaching photoinitiating groups to a polymeric or macromolecular structure. The photoinitiating groups, when exposed to light of the appropriate wavelength, will undergo photoinduced scission and generating radicals which are retained on the polymeric or macromolecular structure. These retained radicals then initiate, terminate, or, in some other way participate in the gel forming process that is the objective of the radiation cure of the photomaterial. Each polymeric or macromolecular photocrosslinking molecule has many more than one photoinitiating groups within its structure, and thus it provides a number of crosslinking sites.

The photocrosslinkers according to the present invention can be employed in different systems.

According to a first aspect, they can be employed in a conventional monomer composition, wherein they may be able to replace conventional crosslinking agents in the system.

According to a second highly advantageous application the inventive crosslinkers are employed in a water based composition of hydrophilic crosslinkable units, as exemplified by hydrophilic or water soluble macromolecular particles provided with functional vinylic, acrylic or methacrylic groups for crosslinking to a solid gel with a defined modulus. This type of systems are described in more detail in our parallel patent applications claiming priority from the Swedish Patent Application SE 9800853. However, it is to be understood that the inventive photocrosslinkers are equally applicable on other types of completely or partially polymerized systems which are to be crosslinked into a final product. The mentioned water based systems are especially preferred in the preparation of such medical products which must undergo final crosslinking *in vivo* in the human body. According to a preferred aspect of the present invention, the photocrosslinkers therefore comprise photoinitiating groups attached to a polymeric or macromolecular structure having such overall characteristics that the photocrosslinkers become water soluble. Therefore, the polymeric or macromolecular part of the photocrosslinkers, preferably should include at least one unit with a suitable hydrophilicity. Suitable units are selected among, but not limited to, N-vinylpyrrolidone (NVP), 2-

hydroxyethylmethacrylate, N-N-dimethyl-acrylamide and vinylactate. It is also referred to Table 1 below in the exemplifying part of the description for a number of specific photocrosslinkers based on such units (or co-monomers) and 4-vinylbenzoyl-diphenylphosphine oxide (VBPO) as a photoinitiating group. Accordingly, units C in general formula above are constituted by VBPO units.

Some especially suitable water soluble, blue light activated photocrosslinkers according to the present invention comprise NVP together with vinyl acetate units, N,N-dimethylacrylamide units alone or together with 2-hydroxyethylethacrylate units, all combined with VBPO units. These photocrosslinkers demonstrate high conversion rate (monomer to polymer) and suitably high stability in aqueous solution.

It is to be understood that the skilled person readily can arrive with alternatives and complements to the mentioned units (co-monomers) for specific purposes in a specific technical application as long as the mentioned general requirements are met.

According to another embodiment of the present invention, the photocrosslinkers are adapted to crosslink silicone based systems. A suitable silicone system is described in the Swedish Patent Application No. 9803481 which comprises an acryl-terminated siloxane copolymer capable of being photopolymerized with a blue light photoinitiator. Suitable photocrosslinkers for silicone based systems preferably comprises photoactive groups according to above, attached to a macromolecule comprising the mentioned siloxane units.

The use of a photocrosslinker confers distinct advantages, both chemical and environmental, as compared with the combination of a separate photoinitiator and crosslinker. In a chemical context the use of a photocrosslinker gives opportunities to produce networks that are more homogeneous than those produced by photocuring conventional photocurable systems. The latter systems, involving as they do, combinations of monomers, have structures dependent on the reactivity ratios of the monomers and crosslinkers. Often, for example, in a coating being manufactured at high rates of production, a crosslinker is selected because of its high reactivity. Disparities in the reactivities of the components of a formulation gives rise to compositional drift, the change of the average unit composition during the course of a polymerization, and this in relation to a reactive crosslinker implies that sections of a network forming later, in the curing process, have a lower crosslink density than

sections formed earlier. Improving the homogeneity of crosslinked networks is a subject receiving greater attention as the technical demands imposed on industrial products increases. Homogenous networks have, for example, higher fracture toughness and better optical properties heterogeneous networks. The shrinkage occurring during their formation is more uniform allowing for more precision in castings. The benefits of using a photocrosslinker as a network former, as compared with a combination of photoinitiator and crosslinker, arise because the radical species they produce act as crosslinkers *via* the polymer chain to which they are attached. Further such radicals are generated throughout the setting phase, their concentration being controlled by the photoinitiating species' quantum efficiency and the intensity of the light, which may be modulated during the setting, in addition to its concentration. This distinction results in the formation of networks having a more controlled and homogeneous structure.

Retaining photoinitiator residues in the network of a medical product, such as a contact lens or a dental filling has desirable physiological implications. Further photocrosslinkers because of their polymeric, or macromolecular, nature are more acceptable, environmentally, than many conventional crosslinkers which are known to cause skin and lung irritation.

Within the context of the present invention, it is possible to substitute a photocrosslinker, either completely, or partially, for a combination of a conventional photoinitiator and a conventional crosslinker. Alternatively, the inventive photocrosslinkers can be used in combination with a conventional photoinitiator or a conventional crosslinker as will be understood by practitioners skilled in formulating systems for crosslinking.

Persons skilled in this art will also appreciate that the inventive photocrosslinkers as described herein for photoactive systems responsive to visible light may be applied equally to systems responsive to UV light, so the present invention is of very general applicability.

Detailed and exemplifying description of the invention

Example 1

This examples shows conceivable structures of photocrosslinkers for use in different systems including silicon based systems.

$$(-CH_2-\overset{R^1}{\underset{R^2}{C}}-)_n\ (CH_2-\overset{R^1}{\underset{R^3}{C}}-)_m\ (CH_2-\overset{R^1}{\underset{R^4}{C}}-)_p$$

R^1= H or CH_3-;

R^2 = e.g. -$CON(Me)_2$, -$CO_2CH_2CH_2OH$, -$OCOCH_3$, -OH, etc.

R^3 as R^2, but R^3 does not = R^2

$$R^4 = -PhCO\overset{Ph}{\underset{R}{P}}=O \quad \text{or}$$

$$-PhPO\overset{Ph}{\underset{R^5}{C}}=O$$

where R^5 = phenyl or styryl

n = 0 - 98 mole%; m = 0 - 98mole%

n + m = 50 - 98 mole%

p = 0.5 - 50 mole%

or

$$(-Si\overset{R^1}{\underset{R^2}{}}-O-)_n\ (-Si\overset{R^1}{\underset{R^3}{}}-O-)_m\ (-Si\overset{R^1}{\underset{R^4}{}}-O-)_p$$

R^1= CH_3-;

R^2= Ph or CH_3-;

R^3= R^1 or R^2 or $CF_3(CH_2)_2$-;

R^4 and R^5 are as above; and

n, m and p are as above.

Example 2

PHOTOCROSSLINKER POLYMER PREPARATIONS

Table 1

photocrosslinkers	VBPO (mole%)[1]	Comonomer 1 (mole%)	Comonomer 2 (mole%)
P31-1	3.5	HEMA(5)	NVP(91.5)
P32-1	3.5	VAc(10)	NVP(86.5)
P40-3	4	DMA(96)	none
P40-4	4	PEMA(96)	none
P41-1	6	DMA(94)	none

The following Examples describe the preparation of P32-1(3), P40-3 & P41-1 (comparison), and P40-4 respectively.

Example 2A

Photocrosslinker Copolymer employing N-Vinylpyrrolidone and Vinyl acetate

This preparation, on an 8 g monomer scale, used monomers in the molar ratio: 86.5 parts N-vinylpyrrolidone (VP): 10 parts vinyl acetate (VAc): 3.5 parts vinylbenzoyldiphenylphosphine oxide (VBPO).

Methoxydiphenylphosphine, 0.520 g, was weighed to a dried 100 ml twin-neck flask, with one neck septum sealed, and coated in aluminum foil to exclude light. Toluene, 3 ml, and a magnetic stir bar were added and the flask flushed with dry nitrogen. The stopcock was briefly removed and 4-vinylbenzoyl chloride, 0.409 g, added, the flask being again flushed with dry nitrogen, then placed in a bath at 65°C, with magnetic stirring.

After 15 minutes, the other monomers: VP, 6.620 g, and VAc, 0.595 g, were diluted with a previously prepared solution of azobisisobutyronitrile (AIBN),

0.080 g in 8 ml toluene, and the mixture injected to the flask and rinsed in with a further 4ml toluene. The polymerization mixture was heated at 65°C with magnetic stirring for 8 hours, yielding a clear pale yellow solution which was precipitated, in subdued light, to diethyl ether. The supernatant was discarded and the pale sludge-like precipitate taken up in 30 ml methanol and reprecipitated to ether as a curdy precipitate. The supernatant was decanted, and the polymer product dried to constant weight under vacuum at 35°C . Yield was 5.751 g (72%) of friable pale yellow polymer. Elemental analysis gave 0.65% P, corresponding to 6.9 %ww VBPO units (0.209 mmol/g), and 10.70% N, corresponding to 84.5 %ww VP units, and thus a mean unit mass of 115 Daltons. SEC gave M_n 32,000 , M_w 103,000. This implies a number average chain length of ca.280 units, with ca.7 photoactive units per chain.

Example 2B

Photocrosslinker Copolymer employing N-Dimethylacrylamide (I)

In this example, 4-vinylbenzoyldiphenylphosphine oxide (VBPO), 4 mol%, was copolymerized with N,N-dimethylacrylamide (DMA), 96 mol%, on a 6 g scale.

Methoxydiphenylphosphine, 0.481 g, was weighed to a dried 24x150mm Quickfit tube, and 2.5 ml dry toluene added. The tube was then wrapped in aluminum foil to exclude light. 4-Vinylbenzoyl chloride, 0.368 g, and a magnetic stir bar were added, and the tube septum sealed, N_2 flushed, and placed in a bath at 65°C with stirring. After 15 minutes a solution of DMA, 5.26g, and AIBN, 0.060g, in toluene, 5ml, was injected by syringe and rinsed in with a further 3.6ml toluene. The mixture was stirred 6 h at 65°C, yielding a viscous orange-yellow solution, which was diluted with methanol and precipitated in diethyl ether. The product was reprecipitated from methanol to ether, and vacuum desiccated at room temperature. Yield, 2.56 g (43%) of friable pale yellow polymer, analysis 0.82% P corresponding to 8.8 %ww VBPO units (0.265 mmol/g).

Example 2C

Photocrosslinker Copolymer employing N-Dimethylacrylamide (II)

Example 2B was repeated on a 12 g scale, but with monomer ratio 6 mol% VBPO (2.12 g), 94 mol% DMA (9.89 g), with 0.120 g AIBN, 22.3 ml toluene, and polymerization time extended to 8h at 65°C. The yield was 7.17g (60%) of yellow polymer, analysis 1.49% P corresponding to 16.0 %ww VBPO (0.481mmol/g).

Example 2D

Photocrosslinker Copolymer employing 2-Phenylethyl methacrylate

In this example, 4-vinylbenzoyldiphenylphosphine oxide (VBPO), 4 mol%, was copolymerized with 2-phenylethyl methacrylate (PEMA), 96 mol%, on a 6 g scale.

Methoxydiphenylphosphine, 0.271 g, was weighed to a dried 24x150mm Quickfit tube, and 2.5 ml dry toluene added. The tube was then wrapped in aluminum foil to exclude light. 4-Vinylbenzoyl chloride, 0.204 g, and a magnetic stir bar were added, and the tube septum sealed, N_2 flushed, and placed in a bath at 65°C with stirring. After 15 minutes a solution of PEMA, 5.60 g, and AIBN, 0.060 g, in toluene, 5ml, was injected by syringe and rinsed in with a further 3.6ml toluene. The mixture was stirred 6 h at 65°C, yielding a fairly viscous pale yellow solution, which was diluted with chloroform and precipitated to methanol. The product was reprecipitated from chloroform (with THF added to clarify the solution), and vacuum desiccated at room temperature. Yield, 4.67 g (78%) of friable pale yellow polymer, analysis 0.48% P corresponding to 5.2 %ww VBPO units (0.155 mmol/g).

Example 3

The following examples refer to photopolymerization including the inventive photocrosslinkers compared with photopolymerization with commercially available photoinitiators.

Example 3A

The state of the art photoinitiator Irgacure 1800 (ex Ciba-Geigy, 10.0mg) was dissolved, in subdued light, in 2-hydroxyethylmethacrylate (HEMA, ophthalmic grade ex Polysciences, 970 mg) and 1,6-dihydroxyhexane diacrylate (HDDA, ex , 20.0 mg), and a 10.0 mg sample pipetted into an open DSC aluminum sample pan. The sample pan, covered with a cover-slip of thin glass, was placed in the sample position of the head of a TA Instruments Differential Photocalorimeter (DPC). The temperature of the head was allowed to stabilize under N_2 at 37°C (or in some cases 23°, and the sample irradiated with blue light at an intensity of 8-9 $mWcm^{-2}$.

The area of the polymerization exotherm was determined by conventional computation and the Jg^{-1} of monomer calculated. From the Jg^{-1} the percentage conversion of monomer to polymer was calculated using a literature value for the latent heat of polymerization of the monomer, ΔH_p. The findings are collected in Table 2.

Using the same composition as was used for the DPC tests discs (2mm thick x 16mm diameter) of polyHEMA were cast in PTFE casting cells. About 500mg of the mixture of monomers and photoinitiator were introduced into the cell which was closed with a glass slide and irradiated with blue light, either from a blue light dental gun, or from a proprietary light generator (Efos Novacure), for 3min.

Example 3B

The method described in Example 3A was repeated using with the state of the art photoinitiator Lucirin TPO (ex BASF, 10.0mg) instead of Irgacure 1800.

Example 3C

The method described in *Example 3A* was repeated using HEMA (900.0mg), no HDDA, and, instead of Irgacure 1800, a photocrosslinker according to the present invention (P31-1, see Table1. for composition, 100.0mg)

Example 3D

The method described in *Example 3C* was repeated using a photocrosslinker according to the present invention (P32-1, see Table 1. for composition, 100.0mg).

Example 3E

The method described in *Example 3C* was repeated using a photocrosslinker according to the present invention (P40-3, see Table 1. for composition, 100.0mg).

Example 3F

The method described in *Example 3C* was repeated using a photocrosslinker according to the present invention (P41-1, see Table 1. for composition, 100.0mg).

Example 3G

The method described in *Example 3A* was repeated using a photocrosslinker according to the present invention (P32-1, 100.0mg) instead of Irgacure 1800, HEMA (600.0mg), water(300mg) and no HDDA.

Example 3H

As *Example 3G*, using P40-3 (50.0mg) to replace P32-1, and HEMA (500.0mg), water (450.0mg).

Example 3I

As *Example 3H* using P41-1(50.0mg) to replace P40-3.

Example 3J

The method described in *Example 3A* was repeated using 2-phenylethylacrylate (PEA, 990.0mg, ex Polymer & Dajac Laboratories) instead of HEMA and no HDDA.

Example 3K

The method described in *Example 3A* was repeated using instead of Irgacure 1800 a photocrosslinker (P40-4, see Table 1. for composition, 100.0mg) and PEA (900mg) but no HDDA or HEMA.

The % conversions of monomer to polymer in Table 2., Examples 3A and 3B, the commercial photoinitiators, and the photocrosslinkers, Examples 3C to 3E, are comparable showing that the photocrosslinkers behave as efficient photoinitiators, especially giving regard to the concentrations of photoactive species, the acylphosphine oxide (shown in Table 1) Further when these findings are compared with Examples 3G to 3I the comparison reveals that correctly designed photocrosslinkers (Examples 3H and 3I) exhibit 100% conversions in solution in water.

For the 2-phenylethylacrylate monomer the photocrosslinker P40-4, based on 2-phenylethylmethacrylate, is also very efficient as a photoinitiator (comparing Examples 3J and 3K) giving 100% conversion of monomer to polymer gel, as judged from the heat of polymerization (based on experimentally determined ΔH_p).

Table 2. A comparison of the completeness of blue light photopolymerisation of HEMA, HEMA in water, & PEA using low molecular weight photoinitiators and photocrosslinkers

Ex. No.	**Formulation**[a] (wt%)[m.eq photoactive ingredient[b]/100g]	**Heat of Polym.** (Jg^{-1})	**Polym. time** (min)	**Conversion** %
3A	HEMA(97)HDDA(2)I1800(1)[0.51]	351	3.5	80
3B	HEMA(97)HDDA(2)TPO(1)[2.9]	357	1.5	82
3C	HEMA(90)P31-1(10)[2.0]	308	6	70
3D	HEMA(90)P32-1(10)[2.3]	309	3	71
3E	HEMA(90)P40-3(10)[2.7]	307	2	70
3F	HEMA(90)P41-1(10)[4.8]	361	1.5	82
3G	HEMA(60)H_2O(30)P32-1(10)[2.3]	>275	>7	>63
3H	HEMA(50)H_2O(45)P40-3(5)[1.4]	452	7	100(approx.)
3I	HEMA(50)H_2O(45)P41-1(5)[2.4]	454	6	100(approx.)
3J	PEA(99)I1800(1)[0.51]	455	2.5	100(approx.)
3K	PEA(90)P40-4(10)[1.6]	456	3.5	100(approx.)

[a]Photocrosslinkers, and monomer HEMA, as Table 1.: commercial photoinitiators I1800, bis(2,6-dimethoxybenzoyl)-trimethylpentylphosphine oxide (25%) + 1-hydroxy-cyclohexylphenylketone (75%)(Irgacure 1800 ex Ciba-Geigy)
TPO, 1,3,5-trimethylbenzoyldiphenylphosphine oxide (Lucirin TPO ex BASF): monomer PEA, 2-phenylethylacrylate: crosslinker HDDA, hexan-1,6-diol diacrylate
[b]m.eq. of acylphosphine oxide/100g of formulation.

Example 4

Examples for Gelation Tests:

Examples 4A and 4B

Using the formulations described above in Examples 3J and 3K and the casting method described in *Example 3A* discs were prepared.

Example 4C

Irgacure 2959 (ex Ciba-Geigy, 10.0 mg) was dissolved, in subdued lighting, in 2-hydroxyethylmethacrylate (HEMA, ophthalmic grade ex Polysciences, 550.0 mg) and water (440.0 mg). Test discs (2mm thick x 16mm diameter) of polymer were cast in PTFE casting cells. About 800mg of the mixture of monomers and photoinitiator were introduced into the cell which was closed with a glass slide and irradiated with light from a proprietary light generator (Efos Novacure), for 3 min.

Example 4D

As *Example 4C* with Irgacure 2959 (30.0 mg), HEMA (540.0 mg) and water (430.0 mg).

Example 4E

As *Example 4C* with P40-3 (100.0 mg) replacing Irgacure 2959, HEMA (500.0mg), and water (400.0mg).

Example 4F

As *Example 4C* with P41-1 (70.0mg) replacing Irgacure 2959, HEMA (510.0mg), and water (420.0mg).

Example 4G

As *Example 4C* with P40-4 (50.0mg) replacing Irgacure 1800, PEA (900.0mg), and additional crosslinker, CE7-2 (2-phenylethylmethacrylate/2-hydroxy-3-acryloxypropylmethacrylate

copolymer [0.9:0.1 mole ratio], 50.0mg).

Example 4H

As *Example 4G* with Irgacure 1800 (21.0mg) replacing P40-4, PEA (940.0mg), and crosslinker, CE7-2 (2-phenylethylmethacrylate/2-hydroxy-3-acryloxypropylmethacrylate copolymer [0.9:0.1 mole ratio], 60.0mg).

Example 4I

As *Example 4B* with PEA (750.0mg), and photocrosslinker, P40-4 (250.0mg).

In Table 3. are collected the tests made to check the gelation of the different formulations. Where a composition is gelled it does not dissolve in solvent, but swells to an extent related to its crosslink density. Uncrosslinked (sol) polymers dissolve.

Examples of monomers photopolymerized with conventional photoinitiators of low molecular weight, nos. 4A, 4C and 4D dissolved readily in the appropriate solvent, water for polyHEMA, and acetone for polyPEA. Example no. 4B showed an intermediate behavior and dissolved partially in acetone leaving some residual gel. Increasing the proportion of photocrosslinker to 25% (3.9m.eq. of acylphosphine oxide, Example 4I or, adding separate crosslinker, CE7-2 (Example 4G, see below) produced acetone insoluble gel.

CE7-2, a polyPEMA which is unsaturated and PEA miscible, being a copolymer of 2-phenylethylmethacrylate/2-hydroxy-3-acryloxypropylmethacrylate [0.9:0.1 mole ratio], was employed as a supplementary crosslinker to the photocrosslinker P40-4, in Examples 4G and 4H. That CE7-2 is an effective cross-linker for photopolymerized PEA is demonstrated in example no. 4H, where in combination with Irgacure 1800 it also yields a gelled product upon irradiation. The products upon irradiation are transparent gelled elastomers of high refractive index (RI>1.54), similar in properties to PEA/PEMA copolymers.

Examples 4E and 4F which used photocrosslinkers to replace conventional

photoinitiators for HEMA/water compositions were gelled and did not dissolve in water, unlike examples 4D and 4E.

Table 3. Gelation tests on photopolymerized materials, shewing effect of photocrosslinkers

Ex. No.	Formulation (wt%)[1]	Effect of Solvent	Comments
4A	PEA(99)I1800(1)	Dissolves in Acetone	Not Crosslinked
4B	PEA(90)P40-4(10)	Dissolves & Swells in Acetone	Lightly Crosslinked
4C	HEMA(55)H_2O(44)I2959[2](1)	Dissolves in Water	Not Crosslinked
4D	HEMA(54)H_2O(43)I2959(3)	Dissolves in Water	Not Crosslinked
4E	HEMA(50)H_2O(40)P40-3(10)	Swells in Water	Crosslinked Gel
4F	HEMA(51)H_2O(42)P41-1(7)	Swells in Water	Crosslinked Gel
4G	PEA(90)CE7-2(5)P40-4(5)	Swells in Acetone	Crosslinked Gel
4H	PEA(94)CE7-2(6)I1800(2.1)	Swells in Acetone	Crosslinked Gel
4I	PEA(75)P40-4(25)	Swells in Acetone	Crosslinked Gel

[1] See Tables 1. & 2., and text for an explanation of materials codes
[2] I2959, 2-hydroxy-4'-hydroxyethoxy-2-propiophenone (UV curing)

The crosslinked structure of the water swollen hydrogels (4E and 4F) was confirmed by stress relaxation tests.

Claims

1. Macromolecular photoinitiator compounds having a general formula

$(A)_n(B)_m(C)_p$

capable of participating in a crosslinking photoinitiated reaction with a substrate having groups active for crosslinking, wherein A, B and C are units either of substituted ethylene groups or substituted siloxane groups in the macromolecular structure and wherein:

(i) the units A, B, C do not have same substitutions;
(ii) the unit C is linked to a photoactive group;
(iii) said photoactive group generates radicals retained on the macromolecular photoinitiator when exposed to light at a determined wavelength in order to accomplish a crosslinking reaction with the substrate; and wherein
(iv) n = 0-98 mole %, m = 0-98 mole %, n+m = 50-98 mole % and p = 0.5-50 mole %.

2. Macromolecules according to claim 1 characterized in that the photoactive group generates free radicals by irradiation of light having a wavelength above 305 nm.

3. Macromolecules according to claim 2 characterized in that the photoactive group comprises a phosphorous atom.

4. Macromolecules according to claim 1 or 2 characterized in that the photoactive group is linked to units C by an acyl- or aroyl group.

5. Macromolecules according to claim 4 characterized in that the links to the units C comprise an optionally substituted phenylene group.

6. Macromolecules according to claim 1, wherein the units A, B, C of the macromolecular photoinitiator structure are:

A= $-CH_2-C(R^1R^2)-$, B= $-CH_2-C(R^1R^3)-$, C= $-CH_2-C(R^1R^4)-$, wherein

R^1 is hydrogen or methyl;

R^2 is $-CON(Me)_2$, $-CO_2CH_2CH_2OH$, $-OCOCH_3$, $-OCOCH_2CH_2Ph$, -OH or a lactam group;

R^3 is $-CON(Me)_2$, $-CO_2CH_2CH_2OH$, $-OCOCH_3$, $-OCOCH_2CH_2Ph$, -OH or a lactam group when B is $-CH_2-C(R^1R^3)-$ with the proviso that R^2 and R^3 are not the same; and

R^4 = -PhCOP(Ph)(R^5)=O or -PhP(R^5)OC(Ph)=O wherein R^5 = phenyl, 3,5-dimethylphenyl, 3,5-dimethoxyphenyl, 3,5-dimethylolphenyl or styryl.

7. Macromolecules according to claim 6, wherein R^2 and R^3 are selected so as to form a water soluble molecule.

8. Macromolecules according to claim 6, wherein said lactam units together with units A or B constitute N-vinylpyrrolidone units.

9. Macromolecules according to claim 1, wherein the units A, B, C of the macromolecular photoinitiator structure are:

A= $-Si(R^1R^2)-O-$, B= $-Si(R^1R^3)-O-$ and C= $-Si(R^1R^4)-O-$, wherein

R^1 is $-CH_3$;

R^2 is methyl or phenyl;

R^3 is R^1, R^2 or $-CH_2CH_2CF_3$;

R^4 = -PhCOP(Ph)(R^5)=O or -PhP(R^5)OC(Ph)=O wherein R^5 = phenyl, 3,5-dimethylphenyl, 3,5-dimethoxyphenyl, 3,5-dimethylolphenyl or styryl.

10. A method of crosslinking an aqueous solution comprising discreet crosslinkable units characterized by mixing the solution with water soluble photoactive macromolecules according to any of claims 1 to 8 and irradiating it with light for a time sufficient to form a solid article.

11. A method of crosslinking according to claim 1, wherein said crosslinkable units are water soluble macromolecular particles provided with functional groups for crosslinking.

12. A method according to claim 12, wherein said functional groups are selected among vinylic, acrylic and methacrylic groups.

13. A method according to claim 10 wherein a lens for ophthalmic use is produced.

14. A method of crosslinking a solution comprising monomers characterized by mixing the solution with photoactive macromolecules according to any of claims 1 to 8 which are soluble in said solution and irradiating it with light for a time sufficient to form a solid article.

15. A method according claim 14, wherein said solution comprises vinylic, acrylic or methacrylic monomers.

16. A method according to claim 14, wherein the solution further comprises macromolecular particles provided with functional groups for crosslinking.

17. A method according to claim 14, wherein a lens for ophthalmic use is produced.

18. A method of crosslinking a silicone composition characterized by mixing composition with photoactive macromolecules according to claims 1 or 9 and irradiating it with light for a time sufficient to form a solid article.

19. A method according to claim 18, wherein said silicone composition comprises siloxane copolymer having functional acrylic groups for crosslinking.

20. A method according to claim 18, wherein a lens for ophthalmic use is produced.

21. A method according to any of claims 10 to 19 characterized by irradiation with light of a wavelength above 305 nm.

Abstract

The present invention relates to new macromolecular compounds with photoinitiator properties, capable of acting as photocrosslinkers providing a combination of photoinitiating and crosslinking processes.